

DITZEL et al.  
Appl. No. 10/529,723  
December 4, 2008

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DEC 04 2008

### **REMARKS/ARGUMENTS**

Reconsideration of this application is requested. Claims 1-5, 7, 8, 10, 12, 31-36 and 48-51 are in the case.

#### **I. THE OBVIOUSNESS REJECTION**

Claims 1-14 and 31-40 stand rejected under 35 U.S.C. §103(a) as allegedly unpatentable over U.S. Patent 6,258,978 to Kitchen *et al.* (Kitchen). The rejection is respectfully traversed.

As noted in the application as filed, it has been found that when catalysts suitable for use in the production of alkenyl carboxylates, such as vinyl acetate, are exposed to alkene in the absence or substantial absence of molecular oxygen, the catalyst shows unexpectedly low activity during process upsets or shut-down of the process. In addition, benzene production may occur. A need exists therefore for an improved process for producing alkenyl carboxylates in which catalyst inhibition and/or benzene formation are suppressed.

The present invention relates to a process for producing an alkenyl carboxylate in a fluid bed process and, in particular, to steps to be taken during a process upset or shutdown in which the catalyst is exposed to alkene, and optionally carboxylic acid, at low levels of oxygen. The invention seeks to minimize contact of the catalyst with alkene at temperature by reducing the alkene partial pressure or the reaction temperature so as to suppress formation of benzene and/or suppress inhibition of the catalyst.

DITZEL et al.  
Appl. No. 10/529,723  
December 4, 2008

Accordingly, the claimed process provides a fluid bed process for producing an alkenyl carboxylate comprising reacting an alkene, a carboxylic acid and a molecular oxygen-containing gas in a reaction zone in the presence of a catalyst at an elevated reaction temperature,  $T$ , to produce an outlet stream from the reaction zone comprising alkenyl carboxylate and oxygen, wherein during a process upset or shut-down, when the catalyst is contacted with the alkene, at a partial pressure,  $P$ , optionally in the presence of the carboxylic acid, and the outlet stream comprises less than 2vol% oxygen, the partial pressure of the alkene is reduced to at least 50% less than  $P$  and/or the reaction temperature is reduced to below  $100^{\circ}\text{C}$  so as to suppress formation of benzene and/or suppress inhibition of the catalyst. The period of time,  $Z$ , during which the catalyst is exposed to the alkene in the presence or absence of the carboxylic acid and at oxygen levels of less than 2 vol % oxygen before the partial pressure of the alkene is reduced to at least 50% less than  $P$  and/or the reaction temperature is reduced to below  $100^{\circ}\text{C}$  is in the range  $>0$  to 12 hours.

The Action continues with interpreting "the outlet stream comprises less than 2 vol% oxygen" as requiring that the percentage oxygen in the outlet stream be maintained at greater than 2% by reducing the alkene partial pressure. However, this feature is **not** a requirement of the presently claimed invention. In fact, during the situations to which the present claims apply, the oxygen feed to the reactor would almost certainly be stopped and the oxygen content in the reactor would reduce to zero rapidly thereafter. As a result, the percentage oxygen in the outlet stream would not be maintained at greater than 2%.

DITZEL et al.  
Appl. No. 10/529,723  
December 4, 2008

The Action refers to "the shutdown taught by Kitchen". However, although Kitchen mentions that the reactor may be shutdown if the oxygen level in the outlet stream exceeds a threshold value, Kitchen is otherwise silent as to how a shutdown is performed. At point 7b on page 5 of the Action, it is further argued that the Applicant's process corresponds to a "normal shutdown process in which all material flow is terminated and temperature reduced to ambient." While in order to fully shutdown a reactor it is necessary to cool it and stop all reactant flows, at least with respect to a fluid bed process as now claimed, this is an oversimplified view of the shut-down steps that might be applied.

Prior to the present invention, and for both process upsets and planned shutdowns, the person of ordinary skill in the art would have expected that it would be important to maintain a fluidized bed catalyst under fluidized conditions at high temperature and under ethylene for a significant period of time. To illustrate this further, the two possible types of situation of claim 1 may be considered.

The first is a planned shut-down, e.g., for maintenance of the reactor. This will eventually require the reactor to be cool and purged of reactive gases. The first step in any such shutdown would be removal of all oxygen, which would be achieved by stopping the oxygen feed to the reactor, and allowing any oxygen left in the reactor to be consumed. Once oxygen is removed, however, for a fluidized bed process, it would then have been expected by one of ordinary skill that it was important to maintain reaction temperature and ethylene, and to maintain the bed in a fluidized state under the ethylene for a significant amount of time after oxygen removal. This would not be to ensure oxygen consumption, which would be relatively rapid, but because of the acetic

DITZEL et al.  
Appl. No. 10/529,723  
December 4, 2008

acid present. In particular, if the catalyst de-fluidizes in the presence of acetic acid, the acetic acid causes the catalyst particles to stick together and to the walls and fluidization grid in the bottom of the fluidized bed reactor. This catalyst actually forms a solid lump that is very difficult to remove and can result in significant reactor damage. Therefore, prior to de-fluidization, it is important to remove all acetic acid from the circulating gases. In fact, acetic acid is removed inherently in the recirculation loop by which the fluidizing gases are recirculated to the reactor and, therefore, can be removed by simply allowing the circulation of gases to continue for a long enough time until the catalyst is "dry". However, even after further acetic acid introduction to the reactor is stopped, and even at reaction temperature, this does take a significant amount of time.

Therefore, even for planned shutdowns, prior to the process of the present invention, one of ordinary skill would have planned to allow the ethylene to circulate at high temperature prior to starting to cool the reactor and remove the ethylene. This could easily have been expected to involve a time period upwards of 24 hours before the ethylene partial pressure was reduced and/or the temperature reduced.

Further, the person of ordinary skill might have considered an increase in temperature, rather than cooling, since this would increase the rate of acetic acid removal. Replacement of ethylene with nitrogen during this time would not only be unnecessary, but detrimental, because nitrogen has a much lower heat capacity than ethylene and a much higher viscosity, both of which would hinder acid removal relative to ethylene.

Even with a process upset, such as might cause a "trip" according to the process of Kitchen, the most important response of an operator or emergency shut-down

DITZEL et al.  
Appl. No. 10/529,723  
December 4, 2008

process would have been to stop oxygen addition to the fluidized bed. Once oxygen addition is stopped, the reaction will rapidly consume the oxygen already in the fluidized bed reactor, and the reactor may be considered as "safe". Unless the process upset was caused by a fault that required the reactor to be opened, it would be highly desirable to maintain the bed at reaction temperature and in a fluidized state by continuing to circulate the reaction gases other than oxygen (i.e. alkene, acid and any inert present). In particular, this allows quicker start-up when the fault is fixed. There would have been no motivation for one of ordinary skill to cool the reactor since it would simply need to be heated up again, and no motivation to purge the reactor of alkene since this would result in a significant loss of reactant. Even if the upset was such that the reactor was to be shut-down, for the same reasons as described above, the "normal" shut-down method would have then been followed which would be to stop the acid introduction but allow the ethylene to circulate at reaction temperature a significant period of time prior to starting to cool the reactor and remove the ethylene.

Thus, under any scenarios which might have applied prior to the process of the present invention, the person skilled in the art would have believed that there were significant advantages to maintaining the reactor at pressure and temperature under ethylene. Contrary to this, amended claim 1 requires that the ethylene partial pressure is reduced to less than 50% of its initial value and/or that the temperature of the reactor is reduced to less than 100°C within a period of time, Z, of less than 12 hours.

In summary, prior to the present invention, one of ordinary skill would have believed that it was advantageous to maintain the ethylene partial pressure and high temperature to insure acetic acid removal from the circulating gas before defluidization.

DITZEL et al.  
Appl. No. 10/529,723  
December 4, 2008

In light of this, prior to the present invention, there would have been no motivation for one of ordinary skill to significantly reduce the ethylene partial pressure or temperature within a relatively short period of time, Z, even for a planned shutdown. One of ordinary skill would not therefore have been motivated to arrive at the presently claimed process based on Kitchen. Absent any such motivation, a *prima facie* case of obviousness has not been generated in this case. Reconsideration and withdrawal of the outstanding obviousness rejection are accordingly respectfully requested.

## II. CLAIM AMENDMENTS

Claim 1 has been amended to specify (a) that the process is a fluid bed process, basis for which can be found in previous claim 26, (b) to delete reference to "start-up", (c) to specify that the partial pressure, P, of the alkene is reduced "to at least 50% less than P", basis for which can be found in previous claim 6, (d) to specify that the reaction temperature is "reduced to below 100°C", basis for which can be found in previous claim 11, and (e) to specify that "the period of time, Z, during which the catalyst is exposed to the alkene in the presence or absence of the carboxylic acid and at oxygen levels of less than 2 vol % oxygen before the partial pressure of the alkene is reduced to at least 50% less than P and/or the reaction temperature is reduced to below 100°C is in the range >0 to 12 hours", basis for which can be found in previous claim 13, in conjunction with page 4, lines 7-10 of the application as filed.

Claims 6, 9, 11, 13, 14 and 38 have been canceled without prejudice, and certain of the remaining dependent claims have been amended to be dependent on claim 1 or claim 2. Finally, as there are two claims numbered "37", claims 37-47 have been

DITZEL et al.  
Appl. No. 10/529,723  
December 4, 2008


anceled and replaced by corresponding dependent claims 48-51. No new matter is added.

Favorable action is awaited.

Respectfully submitted,

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